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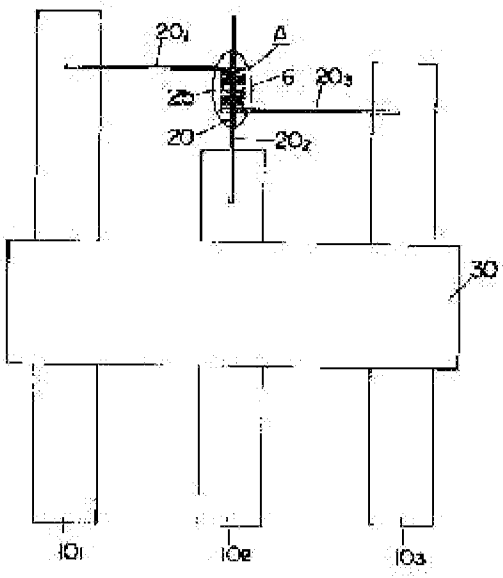
(54) CHLOROFLUOROCARBON SENSOR AND ITS MANUFACTURING METHOD



(57)Abstract:
PROBLEM TO BE SOLVED: To provide a chlorofluorocarbon sensor with high sensitivity and reliability for a fluorocarbon gas.
SOLUTION: In a sensing element A, a heater 25 that is made of the electrode coil of a precious metal wire is buried into a sensitive part 6 that is formed elliptically and at the same time a core 20 that is made of a precious metal wire is provided inside the heater 25. In this case, the heater 25 is provided between lead wires 201 and 203 and the core 20 is formed by a lead wire 202. Also, the lead wire 202 and either of the lead wires 201 and 203 compose an electrode for measuring electrical resistance, and the lead wires 201 and 203 compose an electrode for heating the heater. The sensitive part 6 has SnO2 as a main constituent and is doped with γ-alumina.

CLAIMS

[Claim(s)]
[Claim 1]A chlorofluocarbon sensor which is a chlorofluocarbon sensor which provided an electrode of a couple for electric resistance measurement in an induction part which consists of metal oxide semiconductors, and is characterized by an induction part's using tin oxide as the main ingredients, and coming to add at least one sort in gamma-alumina and formless alumina.
[Claim 2]The chlorofluocarbon sensor according to claim 1, wherein, as for an induction part, total weight contains at least one sort in 0.6wt% thru/or 10wt% of gamma-alumina, and formless alumina to tin oxide.
[Claim 3]A manufacturing method of a chlorofluocarbon sensor which is a manufacturing method of the chlorofluocarbon sensor according to claim 1, and is characterized by forming an

induction part by calcinating by adding alumina sol to tin oxide.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to a chlorofluocarbon sensor.
[0002]
[Description of the Prior Art]Conventionally, the gas sensor using metal oxide semiconductors, such as tin oxide which added the precious metals, such as palladium, as a gas sensitive detector material is used widely.
[0003]
[Problem(s) to be Solved by the Invention]By the way, although the above-mentioned conventional gas sensor detects gas by change of the resistance which occurs when gas contacts the surface of the induction part which uses as the main ingredients tin oxide etc. which are metal oxide semiconductors, there was a problem that the sensitivity to chlorofluocarbon was small. Since the sensitivity of alcohol (ethanol) which is interference gas carried out aging and became high gradually, there was a possibility of becoming a cause of a false report.
[0004]Although research is done by every place about a chlorofluocarbon sensor, for example, it is indicated by JP,57-57249,A, JP,59-120946,A, JP,56-147051,A, JP,1-242951,A, JP,1-242952,A, etc., What has high sensitivity to various chlorofluocarbon by low concentration of 200 ppm or less is not reported.
[0005]Succeeding in this invention in view of the above-mentioned reason, the purpose has the sensitivity to chlorofluocarbon in providing a reliable high chlorofluocarbon sensor.
[0006]
[Means for Solving the Problem]An invention of claim 1 is the chlorofluocarbon sensor which provided an electrode of a couple for electric resistance measurement in an induction part which consists of metal oxide semiconductors to achieve the above objects, and an induction part, Sensitivity to various chlorofluocarbon is high, and tin oxide is used as the main ingredients and it is characterized by coming to add at least one sort in gamma-alumina and formless alumina, since sensitivity of alcohol does not become high temporally, it is reliable, and a false report can be prevented.
[0007]In an invention of claim 1, an induction part is characterized by total weight containing at least one sort in 0.6wt% thru/or 10wt% of gamma-alumina, and formless alumina to tin oxide, and an invention of claim 2 is a desirable embodiment.
[0008]An invention of claim 3 is a manufacturing method of the chlorofluocarbon sensor according to claim 1, and the induction part can add alumina sol to tin oxide, can be characterized by forming by calcinating, and can provide a reliable chlorofluocarbon sensor with high sensitivity to various chlorofluocarbon.
[0009]
[Embodiment of the Invention]The chlorofluocarbon sensor of this embodiment is provided with the following.
The base 30 made of resin which serves as the pars basilaris ossis occipitalis of the cylinder-like-

object-with-base-like sensor housing 40 as shown in drawing 1 and drawing 2.
Three terminal 10_1 which penetrates the base 30 and projects within and without sensor housing 40, 10_2, 10_3.
Sensing element A supported by carrying out connection fixation of lead 20_1, 20_2, and the 20_3 to terminal 10_1, 10_2, and 10_3.
The wire gauze 41 made from the stainless steel for gas introduction formed in the ceiling surface of the sensor housing 40.
While the heater 25 which becomes the induction part 6 in which sensing element A was formed in the shape of an ellipse ball from the electrode coil of a precious-metals line is laid underground, the core wire 20 which becomes an inside of the heater 25 from a precious-metals line is formed. The heater 25 is formed between above-mentioned lead 20_1 and 20_3, and the core wire 20 is formed here of above-mentioned lead 20_2. The electrode for electric resistance measurement is constituted from either one of lead 20_2 or **, and lead 20_1 and lead 20_3 constitute the electrode for heater heating. [lead 20_1 and 20_3] The outside dimension of the induction part 6 sets the path of a longitudinal direction to about 0.5 mm, and has set the path of the transverse direction to about 0.3 mm.
[0010]By the way, the induction part 6 uses SnO_2 as the main ingredients, and has added gamma-alumina.
[0011]Here, if adjustment of SnO_2 is explained, the solution of $SnCl_4$ (tin chloride) is first hydrolyzed by NH_3, stannic acid sol is obtained, in the air, this obtained stannic acid sol will be calcinated at 500 ** after wind desiccation for 1 hour, and SnO_2 will be obtained. It impregnates with the aqua regia solution of Pd to this SnO_2, for example, it calcinates in the air at 500 ** for 1 hour, and may be made to make Pd support. Here, the role of Pd is what (it is made quick) the speed of response to various gas is improved for, and may use other precious metals, such as Pt, Rh, and Au, instead of Pd. Next, an equivalent amount of alpha-alumina of 1000 meshes is mixed as aggregate to SnO2 which does not make SnO2 which made the metal which replaces Pd or it as mentioned above support, or these metal support, The admiration gas material which furthermore added the Tell Young Pioneers and was made into paste state is obtained, and this admiration gas material is applied to the heater 25 and the core wire 20, and is calcinated for 3 minutes at 580 ** in the air. then, alumina sol -- admiration -- it adds to atmosphere and the induction part 6 is formed by calcinating for 3 minutes at 525 ** in the air.
[0012]Its sensitivity to various chlorofluocarbon is high, and the induction part 6 in the chlorofluocarbon sensor of this embodiment uses tin oxide as the main ingredients, contains gamma-alumina in tin oxide, since the sensitivity of alcohol does not become high temporally, it is reliable, and a deer can be carried out and it can prevent a false report. Although the reason the sensitivity to various chlorofluocarbon becomes high is not clear, since gamma-alumina is a strong substance of activity, when gamma-alumina is added by the induction part 6, it is estimated whether adsorption or combustion is promoted on the induction part 6 surface.
[0013]By the way, although gamma-alumina is added to tin oxide by calcinating after adding alumina sol in this embodiment, gamma-alumina, formless alumina, boehmites, or these mixtures may be directly added instead of being alumina sol.
[0014]By impressing predetermined direct current voltage between 1 pair of terminal 10_1 which the operating temperature of the chlorofluocarbon sensor of this embodiment is 300 ** thru/or about 500 **, and was connected to the heater 25, and 10_2, As the temperature of the induction part 6 turns into temperature of 300 ** thru/or 500 **, it should just use it for it.
[0015]This invention has the feature in the gas sensitive detector material (admiration gas

material) which constitutes the induction part 6, The structure of a chlorofluocarbon sensor is not what is not limited to the structure of drawing 1 and drawing 2, and is limited to sintered body type sensing element A which it is got blocked and shown in drawing 1 and drawing 2, For example, monotonous thick film type sensing element A shown in drawing 3 and drawing 4 may be used, and tubular thick film type sensing element A shown in drawing 5 and drawing 6 may be used.

[0016]At 0.3 mm in thickness, sensing element A shown in drawing 3 and drawing 4 provides the gold electrodes 4A and 4B and the gold electrode 2A for heaters, and 2B in the rear face of the square alumina substrate 1 whose length of one side is 2 mm, as shown in drawing 3 (b), Between the gold electrode 2A and 2B, heater 25' which consists of ruthenium oxide is formed. The gold electrodes 4A and 4B connected by the through hole in the gold electrodes 4A and 4B on the back are formed in the surface of the alumina substrate 1, as shown in drawing 3 (a), and spreading calcination of the gold electrode 4A and the admiration gas material which uses tin oxide (SnO_2) as the main ingredients so that it may continue among 4B is carried out. The reed wire 5 is connected to each electrode 2A by the side of the rear face of this alumina substrate 1, 2B, and 4A and 4B, respectively, and it has connected with the terminal 10 which penetrated the reed wire 5 at the base 30.

[0017]Sensing element A shown in drawing 5 and drawing 6 has printed the counterelectrode (not shown) on the periphery of the cylindrical ceramic tube 7, The induction part 6 is formed on a counterelectrode, the coiled heater 25 is allocated into the ceramic tube 7, the length of shaft orientations forms in 3.5 mm, and the outer diameter is formed in 1.2 mm. The four reed wires 5 connected to the induction part 6 are connected to four of the six terminals 10 penetrated at the base 30, and the both ends of the heater 25 are connected to the remaining terminals 10, respectively.

[0018](Example 1) In this example, after adding alumina sol, drawing 1 and the chlorofluocarbon gas sensor of the structure of drawing 2 in which the induction part 6 was formed were produced by calcinating for 3 minutes at 525 ** in the air. In here, the induction part 6 in the chlorofluocarbon sensor of this example contains 0.6wt% of gamma-alumina to SnO_2.

[0019](Example 2) In this example, after adding alumina sol, drawing 1 and the chlorofluocarbon gas sensor of the structure of drawing 2 in which the induction part 6 was formed were produced by calcinating for 3 minutes at 525 ** in the air. In here, the induction part 6 in the chlorofluocarbon sensor of this example contains 1.5wt% of gamma-alumina to SnO_2.

[0020](Example 3) In this example, after adding alumina sol, drawing 1 and the chlorofluocarbon gas sensor of the structure of drawing 2 in which the induction part 6 was formed were produced by calcinating for 3 minutes at 525 ** in the air. In here, the induction part 6 in the chlorofluocarbon sensor of this example contains 3wt% of gamma-alumina to SnO_2.

[0021](Example 4) In this example, after adding alumina sol, drawing 1 and the chlorofluocarbon gas sensor of the structure of drawing 2 in which the induction part 6 was formed were produced by calcinating for 3 minutes at 525 ** in the air. In here, the induction part 6 in the chlorofluocarbon sensor of this example contains 6wt% of gamma-alumina to SnO_2.

[0022](Example 5) In this example, after adding alumina sol, drawing 1 and the chlorofluocarbon gas sensor of the structure of drawing 2 in which the induction part 6 was formed were produced by calcinating for 3 minutes at 525 ** in the air. In here, the induction part 6 in the chlorofluocarbon sensor of this example contains 10wt% of gamma-alumina to

SnO_2.
[0023](Example 6) In this example, after adding alumina sol, drawing 1 and the chlorofluocarbon gas sensor of the structure of drawing 2 in which the induction part 6 was formed were produced by calcinating for 3 minutes at 525 ** in the air. In here, the induction part 6 in the chlorofluocarbon sensor of this example contains 20wt% of gamma-alumina to SnO_2.
[0024](Example 7) In this example, after adding formless alumina, drawing 1 and the chlorofluocarbon gas sensor of the structure of drawing 2 in which the induction part 6 was formed were produced by calcinating for 3 minutes at 525 ** in the air. In here, the induction part 6 in the chlorofluocarbon sensor of this example contains 0.6wt% of formless alumina to SnO_2.
[0025](Comparative example) In this comparative example, the gas sensor of the structure of drawing 1 which formed the induction part without adding alumina sol, and drawing 2 was produced. That is, the induction part of the gas sensor of this comparative example has not added gamma-alumina.
[0026]Here, the result of having performed characteristic measurement of the comparative example which has not added each above-mentioned Examples 1-6 and alumina sol which added alumina sol is explained with reference to drawing 7 thru/or drawing 12. While constituting a circuit as shown in drawing 13 in characteristic measurement, heating the induction part 6 by making into 0.9(V)s heater voltage V_H which is the direct current voltage impressed among the both ends of the heater 25 and making it the temperature of the induction part 6 be 400 **, The direct current voltage of 5(V)s was impressed as voltage for detection V_C among the both ends of the series circuit of the induction part 6 and load resistance R_L, and the resistance of the induction part 6 was calculated based on both-ends voltage $V_{out[\text{ of load resistance RL }]}$. However, the resistance of load resistance R_L was set to 10 (Komega).
[0027]Drawing 7 and drawing 8 are graphs of the resistance R of the induction part 6 in the inside of the various chlorofluocarbon atmosphere over resistance R_{air} of the induction part 6 in the inside of the air shown comparatively (R/R_{air}), drawing 7 shows Example 1 and drawing 8 shows a comparative example, respectively. The horizontal axis of drawing 7 and drawing 8 is gas concentration, and a vertical axis is R/R_{air}, Solid line I (-) in drawing 7 and drawing 8 is two-dot chain line HO about a measurement result [as opposed to / in dashed line NI (**) / R-12 (CCl_2F_2) for a measurement result / as opposed to / in dashed dotted line Ha (<>) / R-404a for a measurement result / as opposed to / in two-dot chain line RO (**) / R-410a for the measurement result of R-407c]. The measurement result of R-134a (CH_2F-CF_3), Solid line HE (O) shows a measurement result [as opposed to / in dashed line CHI (x) / R-600a (C_4H_{10}) for a measurement result / as opposed to / in dashed dotted line TO (**) / R-290 for the measurement result of R-125 (CF_3-CF_3)], respectively. In here, R/R_{air} shows that sensitivity is so high that a value is small in the same gas concentration.
[0028]By adding and calcinating alumina sol from drawing 7 and the measurement result of drawing 8 shows that the sensitivity to various chlorofluocarbon becomes high compared with the gas sensor of a comparative example with which the direction of the chlorofluocarbon sensor of Example 1 provided with the induction part 6 containing gamma-alumina has not added alumina sol. Drawing 9 shows a list of the measurement data in 100 ppm of various chlorofluocarbon.
[0029]Drawing 10 and drawing 11 are graphs which show the measurement result of aging of the resistance R of the induction part 6 at the time of continuous energization, A horizontal axis

shows energization days, a vertical axis shows the resistance R, drawing 10 shows the measurement result of Example 1 (it is 0.6wt% content about gamma-alumina), and drawing 11 shows the measurement result of Example 3 (gamma-alumina is contained 3%), respectively. ** shows the measurement result of the resistance R of the induction part [in / for the measurement result of the resistance R of the induction part / in / for the measurement result of the resistance R of drawing 10 and the **'s of drawing 11 induction part 6 in the air / 100 ppm R-134a atmosphere / 6 / in ** / 100 ppm ethanol atmosphere] 6, respectively.

[0030]The measurement result shown in drawing 10 and drawing 11 shows that change of the chlorofluocarbon [direction / with much content of gamma-alumina] at the time of long-term continuous energization and the resistance R of the induction part 6 to ethanol is small, and temporal stability is good. It turns out that a direction with much content of gamma-alumina can control high sensitivity-ization to the ethanol at the time of long-term continuous energization.

[0031]In a place. Drawing 12 is what shows the result of having measured the resistance R of the induction part 6 about Examples (the addition concentration of gamma-alumina to SnO_2 was changed in 0wt% thru/or 20wt% of the range) 1-6 and the comparative example which changed various additions of gamma-alumina to tin oxide (SnO_2), ** (-) of drawing 12 shows the measurement result in the inside of 100 ppm ethanol atmosphere, ** (**) in drawing 12 shows the measurement result in the inside of 100 ppm R-134a atmosphere, and ** (<>) in drawing 12 shows the measurement result in the inside of 100 ppm R-125 atmosphere, respectively. From the measurement result shown in drawing 12, the sensitivity to chlorofluocarbon becomes high, so that the addition concentration of gamma-alumina is [the addition concentration of gamma-alumina to SnO_2] large in 0.6wt% thru/or 3wt% of the range, it turns out that sensitivity [as opposed to / in the addition concentration of gamma-alumina / chlorofluocarbon at 3wt% thru/or 20wt% of the range] serves as about 1 law. On the other hand, since there is a possibility that problems, such as exfoliation of the induction part 6, may arise in an above-mentioned monotonous thick film type sensing element or a tubular thick film type sensing element when the addition concentration of gamma-alumina to SnO_2 exceeds 20wt%, It is desirable to add 0.6wt% thru/or 10wt% of gamma-alumina to SnO_2.

[0032]Drawing 14 shows the resistance R of the induction part 6 in the inside of various gas atmospheres about the chlorofluocarbon sensor of Example 7. The horizontal axis of drawing 14 is gas concentration, a vertical axis is the resistance R of the induction part 6, and ** (-) in drawing 14 shows a measurement result [as opposed to / in ** (**) / ethanol for a measurement result / as opposed to / in **() / R-125 for the measurement result of R-134a], respectively. Also in Example 7, drawing 14 shows that it is high sensitivity to chlorofluocarbon.

[0033]

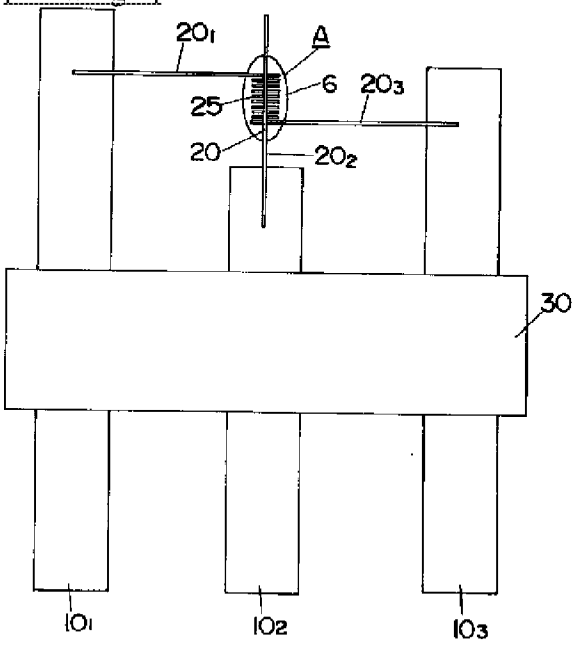
[Effect of the Invention]The invention of claim 1 and claim 2 is the chlorofluocarbon sensor which provided the electrode of the couple for electric resistance measurement in the induction part which consists of metal oxide semiconductors, and an induction part, It is effective in the ability to prevent [since tin oxide is used as the main ingredients and at least one sort in gamma-alumina and formless alumina is added, the sensitivity to various chlorofluocarbon is high, and since the sensitivity of alcohol does not become high temporally, it is reliable, and] a false report.

[0034]The invention of claim 3 is a manufacturing method of the chlorofluocarbon sensor according to claim 1, and an induction part adds alumina sol to tin oxide, and since it forms by calcinating, it is effective in the ability to provide a reliable chlorofluocarbon sensor with high sensitivity to various chlorofluocarbon.

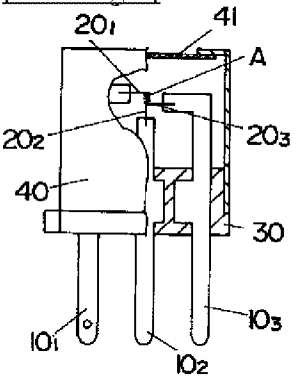
[Translation done.]

DRAWINGS

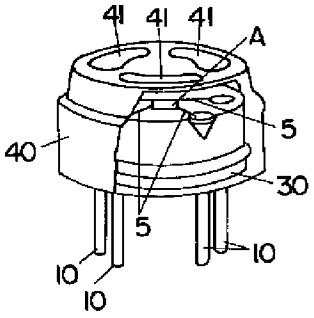
[Drawing 1]



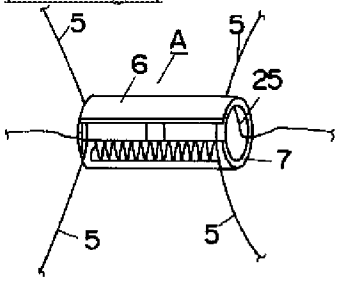
[Drawing 2]



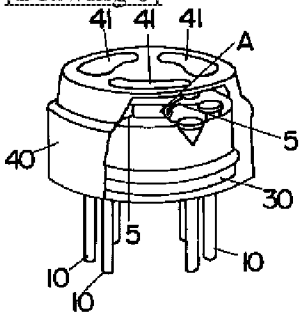
[Drawing 4]



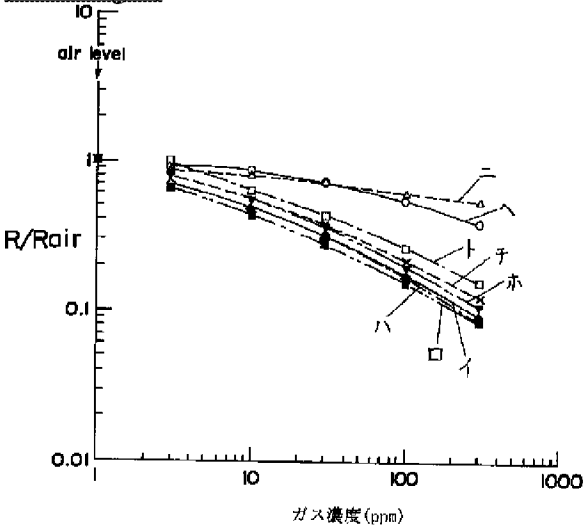
[Drawing 5]



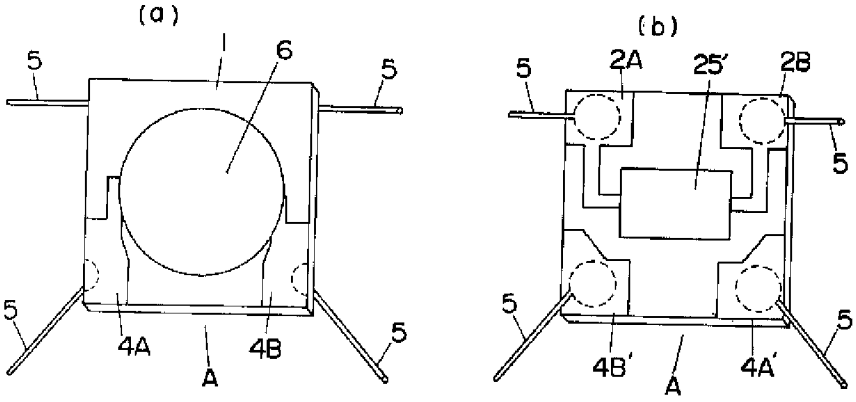
[Drawing 6]



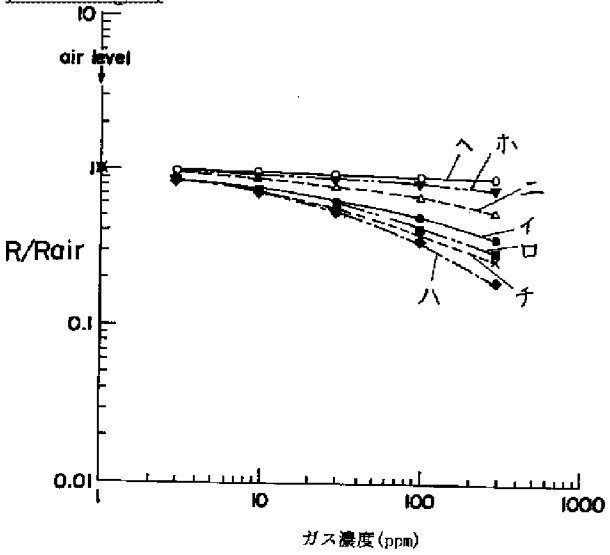
[Drawing 7]



[Drawing 3]



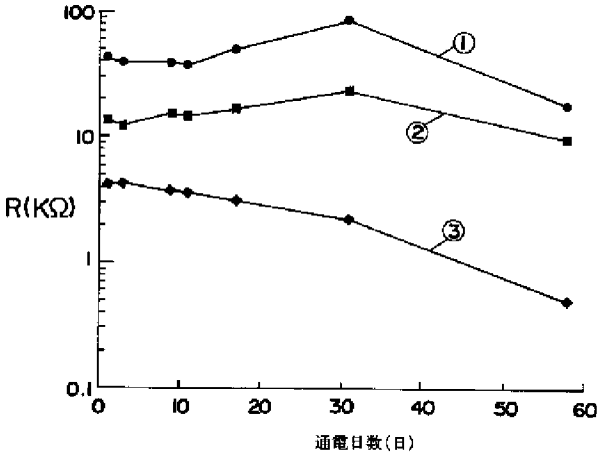
[Drawing 8]



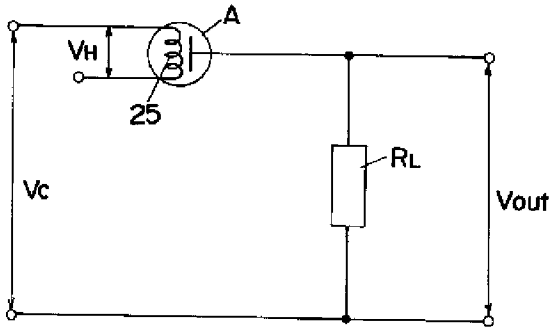
[Drawing 9]

	R-407c	R-410a	R-404a	R-12	R-134a	R-125	R-290	R-600a
アルミナゾル無	0.50	0.42	0.35	0.69	0.84	0.92	0.43	0.38
アルミナゾル有	0.18	0.16	0.17	0.61	0.21	0.56	0.27	0.22

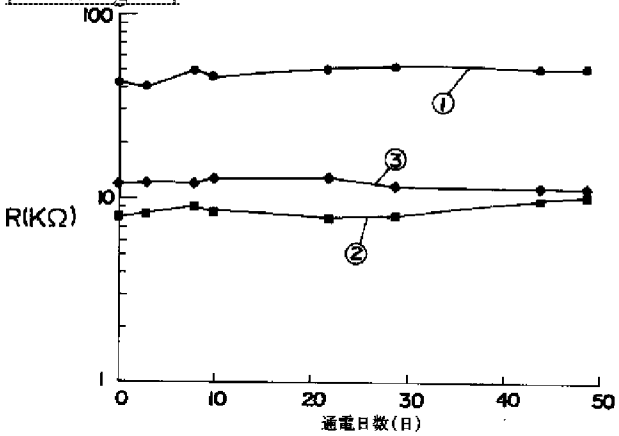
[Drawing 10]



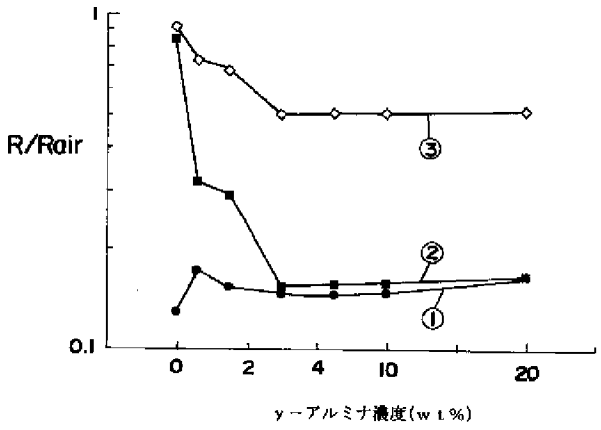
[Drawing 13]



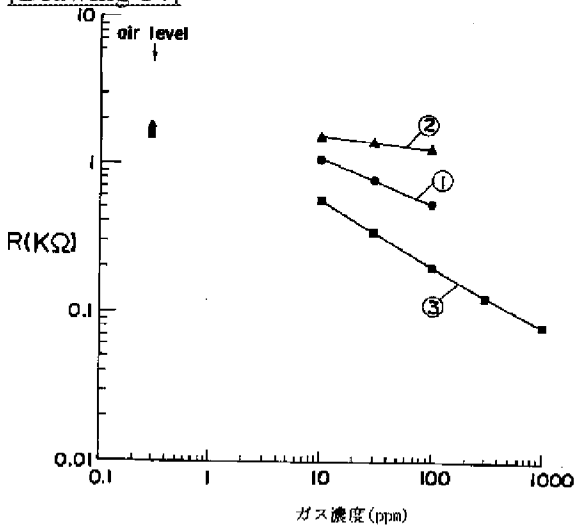
[Drawing 11]



[Drawing 12]



[Drawing 14]



[Translation done.]